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Room temperature deposition of alumina-doped zinc oxide on flexible substrates by direct pulsed laser recrystallization

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In this study, a method combining room temperature pulsed laser deposition (PLD) and direct pulsed laser recrystallization (DPLR) is introduced to deposit transparent conductive oxide (TCO) layer on low melting point flexible substrates. Alumina-doped zinc oxide (AZO), as one of the most promising TCO candidates, has now been widely used in solar cells. However, to achieve optimal, electrical, and optical properties of AZO on low melting point, flexible substrate is challenging. DPLR technique is a scalable, economic, and fast process to remove crystal defects and generate recrystallization at room temperature. It features selective processing by only heating up the TCO thin film and preserve the underlying substrate at low temperature. In this study, AZO thin film is pre-deposited by PLD on flexible and rigid substrates. DPLR is then introduced to achieve a uniform TCO layer on these substrates, i.e., commercialized Kapton polyimide film, micron-thick Al-foil, and sold lime glass (SLG). Both finite element analysis simulation and designed experiments are carried out to demonstrate that DPLR is promising in manufacturing high quality AZO layers without any damage to the underlying flexible substrates. The hall mobility of AZO after DPLR on Kapton and SLG reached $198\,cm^2/v\cdot s$ and $398\,cm^2/v\cdot s$ respectively, while the carrier concentrations are reduced to 2.68×10^{18} and $4.3\times10^{19}/cm^{-2}$, respectively. These characteristics are exactly what an ideal TCO layer should carry: high conductivity and high transmission. The property changes are due to the reduction of defect density after DPLR. [http://dx.doi.org/10.1063/1.3702460]

Cutting-edge flexible solar cells technologies are getting more and more attention in today's solar cells due to their lightweight, robust, portability, and ability to flex, curve, and fold. More importantly, flexible solar cell[1] is more suitable for mass production manufacturing processes such as roll-to-roll printing processes[2] which are very cost efficient. Not only solar cells but also other applications like organic light-emitting diodes (OLEDs)[3] and flat panel displays[4] are also highly dependent on high quality transparent conductive oxide (TCO) layer on flexible substrates. However, many economic flexible substrates, e.g., Kapton, metal thin films, polymers, and even papers, are of relatively lower melting point. They cannot survive from high temperature manufacturing processes, such as elevated temperature sputtering, deposition, and thermal annealing processes. Therefore, lower temperature deposition, sputtering, and thermal annealing techniques are urgently needed for manufacturing high performance flexible solar cells and OLEDs displays. In this study, a method combining room temperature pulsed laser deposition (PLD) and room temperature direct pulsed laser recrystallization (DPLR, Fig. 1(a))[5] are introduced to deposit highly conductive and transparent alumina-doped zinc oxide (AZO, 250 nm) layer on low melting flexible substrates (Kapton polyimide and Al-foil substrates). Both finite element analysis (FEA) modeling and designed experiments have been carried out to demonstrate this process.

Different substrates have different thermal conductivity (κ), substrate crystallinity, and thermal expansion rate. Different resulting AZO film properties, such as film electrical

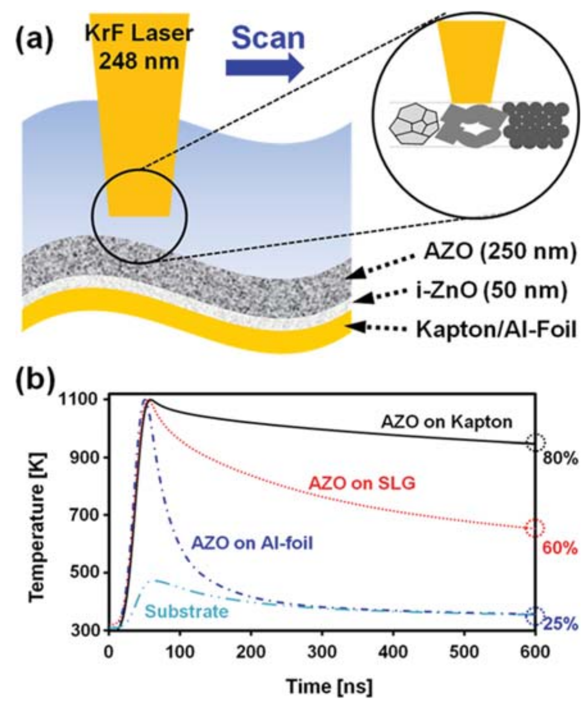

FIG. 1. (a) Schematic of DPLR of AZO film on flexible substrate; (b) Multi-physics model simulates single laser pulse caused temperature profile in AZO film on different substrates. To reach 1100 K (peak temperature), laser fluence used are 50, 60, and 65 mJ/cm^2 for AZO film on Kapton, SLG, and Al-foil substrates, respectively.

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conductivity, AZO crystallinity and internal stress, transmittance, and absorptance are expected. In order to quantify these differences, a multiphysics FEA model is established to analyze the laser-nanoparticle-substrate interactions during DPLR processes. Figure 1(b) depicts that under single pulse DPLR, due to difference of κ, substrate with smaller κ requires smaller laser fluence (F) to reach a temperature comparing with a substrate with larger κ. More details on establishing the FEA model could be found in Ref. 6.

DPLR experiments are also carried out. Before deposition, Kapton, Al-foil substrates and sold lime glass (SLG) are cleaned by acetone, methanol, and DI water in an ultrasonic cleaner, sequentially. ZnO (99.99%) and 2% AZO targets are ablated using a KrF excimer laser (λ of 248 nm with τ of 25 ns). The target/substrate distance is fixed at 80 mm. Targets and substrates rotate at 7 and 5 rpm, respectively. *i*-ZnO film (50 nm) is deposited at laser fluence (F) of 1.5 J/cm^2, repetition rate (RR) of 10 Hz for 20 min. AZO (250 nm) film is deposited at laser fluence of 0.5 J/cm^2, RR of 5 Hz for 90 min. O_2 pressure is set to be 150 and 1 mTorr for *i*-ZnO and AZO films, respectively.

After PLD, the sample is transferred into a 10 mTorr vacuum chamber for room temperature DPLR process. The same laser is used for DPLR with RR of 1 Hz. The laser beam is shaped to square top-hat (8×8 mm). The sample is placed on a motorized stage which enables translations along both X and Y axes. Laser fluence used in DPLR experiments ranges from 15 to 65 mJ/cm^2. The laser pulse number (N) used ranges from 1 to 100.

After DPLR, field emission scanning electron microscopy (SEM) is used to determine the thickness of AZO film via cross-section; top SEM imaging is used to determine the surface structure. X-ray diffraction (XRD) is used to determine AZO film's crystallinity and internal stress. Electrical resistivity, Hall mobility, and carrier concentration density are measured by Hall Effect and Van der Pauw methods. Optical transmittance and absorptance spectra are measured by UV-vis-NIR spectrophotometer. The band gap of AZO is then determined by plotting the absorbance squared versus energy and extrapolating to zero.

Multiphysics simulation and DPLR experiments on peak resulting temperature (T_{peak}) in AZO film on Kapton, SLG, and Al-foil substrates are compared and shown in Table I. Simulation results (Table I and Fig. 1(b)) show that in single pulse scheme, substrate with smallest thermal conductivity (κ) results in highest temperature increase per unit laser fluence ($\Delta T_{peak} = T_{peak} - 300$) and vice versa. This could be explained that Kapton film has the lowest κ, which tends to conducts thermal energy from laser irradiated spot very slowly. When temperature decreases, it decreases faster on higher κ Al-foil substrate (25% of T_{peak} in 600 ns and 300 K in 1 ms) than on smaller κ Kapton (80% of T_{peak} in 600 ns and 60% for 1 ms) and SLG (60% of T_{peak} and 51% for 1 ms).

This phenomenon implies that when multiple pulse scheme is employed, temperature tends to accumulate with number of pulses for AZO on Kapton and SLG substrates, while very little for Al-foil substrate. Therefore, in multiple pulse DPLR experiments, substantially smaller laser fluence is found to be suitable for AZO film deposited on Kapton and SLG substrates (compared with simulation data). As shown in Table I, 25 and 30 mJ/cm^2 are the most appropriate laser fluence for DPLR of AZO on Kapton and SLG, greatly differing from 50 and 60 mJ/cm^2 shown in Fig. 1(b). Corresponding temperature elevations after one laser pulse irradiation are 231 and 398 K.

Assuming that the final temperature of each pulse would stay at 60% and 51% of its T_{peak} when next laser pulse comes, it can be calculated that after 15 laser pulses, T_{peak} in AZO film on Kapton would be 1250 K, and after 30 laser pulses, T_{peak} in AZO film on SLG would be 1224 K. These temperatures are fairly close to melting point of AZO; therefore, recrystallization of AZO are expected. Similar to simulation results, it is found that in DPLR experiments, 15 and 30 laser pulses are needed to best recrystallize AZO thin film deposited on Kapton and SLG substrates. For the case that AZO on Al-foil substrate, since there is no temperature accumulation with laser pulses, 100 laser pulses at fluence of 60 mJ/cm^2 is used in DPLR with corresponding T_{peak} to be $\sim$1038 K.

The AZO crystal size after DPLR processing is strongly depended on substrate's thermal conductivity, where higher conductivity gives larger final AZO crystal size. SEM imaging of top AZO film surface found that after DPLR

TABLE I. Substrate dependence on peak resulting temperature in AZO film as a result of DPLR process.

Substrate	Simulation (single pulse) ΔT_{peak} (K/mJ $\cdot$ cm^{-2})	Experiment (multiple pulse) T_{peak} at Fused	Substrate's thermal conductivity (κ: W/m $\cdot$ K)
Kapton	15.4	685 K at 25 mJ/cm^2	0.12
SLG	13.3	698 K at 30 mJ/cm^2	1.3
Al-foil	12.3	1038 K at 60 mJ/cm^2	250

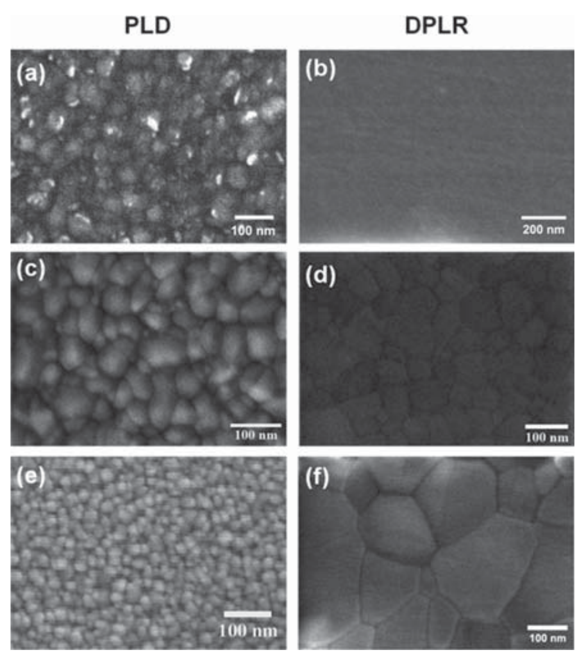

FIG. 2. AZO on Kapton deposited by PLD (a) and processed by 25 mJ/cm^2 with 15 laser pulses (b); AZO on SLG deposited by PLD (c) and processed by 30 mJ/cm^2 with 30 laser pulses (d); AZO on Al-foil deposited by PLD (e) and processed by 60 mJ/cm^2 with 100 laser pulses (f).

processing with its corresponding optimal conditions (see Fig. 2 and Table I), smooth surface with unobvious distinction among crystals are found on Kapton substrate (Fig. 2(a)) and AZO crystals with average size of about 120 nm are found on SLG substrate (Fig. 2(b)), while AZO crystals with size over 300 nm are obtained on Al-foil substrates (Fig. 2(c)).

Temperature distribution in AZO film is believed to be responsible for distinctive difference on AZO crystal size. As discussed above, each laser pulse applied on AZO film deposited on Al-foil substrate would rapidly increase temperature to 1038 K and decrease to 300 K. After 100 pulses, AZO crystals experience 100 cycles of such rapid temperature increase and decrease processes which provide sufficient thermodynamics energy to overcome the grain boundary energy difference and lead to significant growth of AZO crystals. For AZO film deposited on Kapton and SLG, less significant temperature change (thus thermodynamic energy) occurs during the DPLR cycles; therefore, less significant AZO crystal growth is expected.

It is found that as the substrate's crystallinity increases, the crystallinity of the AZO films also increases. In current study, the crystallinity of aluminum (crystalline) is higher than that of Kapton (semi-crystalline) and SLG (amorphous) substrates. Therefore, higher degree of crystallinity is expected in AZO deposited on Al-foil than that on Kapton and SLG as confirmed by XRD spectra analysis (Fig. 3) which illustrates (002) diffraction peak of AZO film processed by DPLR on Al-foil is the sharpest and strongest and that on SLG is the widest and weakest. This indicates that the crystallinity of AZO film deposited on Al foil is better than that of AZO film deposited on Kapton substrate, while the crystallinity of AZO film deposited on SLG substrate is the poorest. This agrees well with the previous findings that the more crystalline the substrate is, the more crystalline the AZO film deposited on the substrate is.[7]

From Fig. 3, a small displacement of the (002) diffraction peak towards a lower angle is observed in AZO film deposited on Kapton (indicating internal tensile film stress), while very minimum amount of displacement of (002) peak is observed in AZO films deposited on SLG and Al-foil. This indicates that after DPLR processing, the film tensile stress is more prominent when AZO is deposited on thermoplastic substrate (Kapton) where thermal expansion occurs. Very little internal stress is found on AZO film deposited on metal (Al-foil) and rigid (SLG) substrates where little thermal expansion of substrate is expected. The presence of film internal tensile stress in AZO film deposited on Kapton substrate may influence its electrical and optical properties and long term device reliability and life time.[8] The previously discovered atomistic peening phenomenon[9] might also be partially responsible for the introduction of tensile stress in the AZO film deposited on Kapton film.

Compared our AZO film on Kapton with earlier reports on AZO film on SLG substrates,[10,11] higher hall mobility and lower carrier density are observed in the AZO film on Kapton processed by current DPLR technique. Although a slightly higher film resistivity is observed which may be ascribed to the intrinsic highly isolative substrate, this indicates that out of all room temperature techniques, DPLR is the most efficient methods to achieve good hall mobility and carrier concentration of TCO layers for thin film solar cell applications.

Measured electrical resistivity of AZO thin film on Kapton substrate after DPLR processing is in the order of $10^{-2}\,\Omega\,\mathrm{cm}$. Compared with DPLR-processed AZO film on SLG, the resistivity of AZO thin film on Kapton is two orders of magnitude lower[5]; this is expected since AZO crystal size found on SLG substrate is bigger than that on Kapton film; larger crystals in thin film usually lead to less internal defects such as inter-grain discontinuities and grain boundaries which give more superior film resistivity. Less internal defects would also lead to higher hall mobility as illustrated in Table II where highest obtained Hall mobility in AZO film on Kapton film is $196.42\,\mathrm{cm^2/v \cdot s}$, while our previous measurements recorded highest Hall mobility of $382.83\,\mathrm{cm^2/v \cdot s}$ for AZO on SLG substrate[5]. However, this would not be a deterministic disadvantage for DPLR since other flexible substrates would always be an option for future works to achieve better crystallinity and thermal properties.

A significant improvement in the near infrared (NIR) region on optical transmittance of AZO film on Kapton is observed after the treatment of DPLR. The higher the transmittance is, the more light the TCO layer would let through, the higher the photon-electron conversion would the thin film solar cell potentially have. Highest improvement on

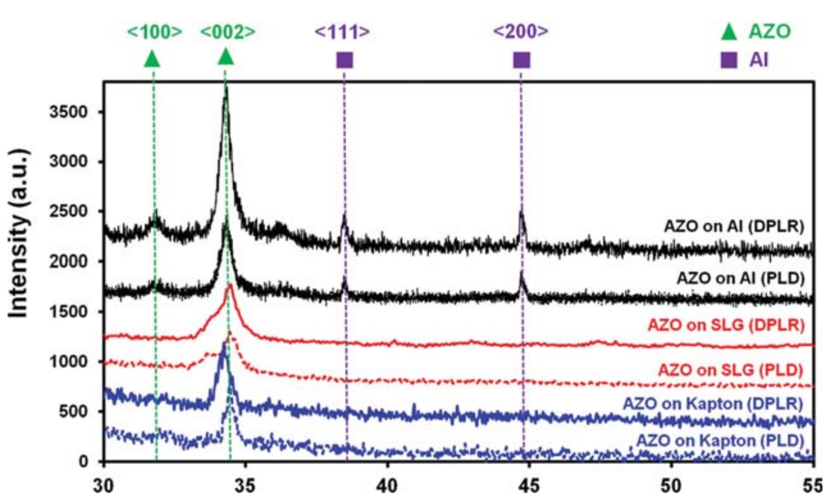

FIG. 3. XRD patterns of AZO on Al-foil, SLG, and Kapton substrates processed by DPLR at optimal conditions, respectively.

TABLE II. Electrical properties of AZO films deposited on Kapton and SLG substrates after DPLR processing. AZO on Kapton was processed by DPLR with $F = 25\,\text{mJ/cm}^2$ and $N = 15$; AZO on SLG was processed by DPLR with $F = 30\,\text{mJ/cm}^2$ and $N = 30$.

Sample	Resistivity (Ω cm)	Hall mobility ($\text{cm}^2/\text{v}\cdot\text{s}$)	Carrier density (cm^{-3})
On Kapton by DPLR_1	1.19×10^{-2}	196.42	2.68×10^{18}
On Kapton by DPLR_2	1.15×10^{-2}	125.61	4.30×10^{18}
On Kapton by DPLR_3	1.15×10^{-2}	25.05	2.16×10^{19}
On SLG by Singh[10]	7×10^{-3}	Not reported	1.56×10^{21}
On SLG by Wang[11]	4.11×10^{-3}	4.6	3.3×10^{20}
On SLG by Zhang[5]	$(2.23 \pm 0.21) \times 10^{-4}$	382.83 ± 1.68	$(4.375 \pm 0.136) \times 10^{19}$

transmittance is with AZO film that was processed by 1 laser pulse at laser fluence of $33\,\text{mJ/cm}^2$ (dash-dotted curve in Fig. 4). From 1000 to 2000 nm, the average enhance on transmittance is 68%, with 4.9% at 1000 nm, 79% at 1500 nm, and 177% at 1980 nm. Less optimal DPLR treatment with 15 laser pulses at $25\,\text{mJ/cm}^2$ (dash curve in Fig. 4) led to an average increase of 11% over the range between 1000 and 2000 nm, with −3% at 1000 nm, 13% at 1500 nm, and 36% at 1980 nm. However if too many laser pulses were delivered (solid curves in Fig. 4), a slightly decrease on transmittance is observed throughout the range under consideration.

In summary, a room temperature processing called DPLR is demonstrated on flexible substrates such as Kapton polyimide film and micrometer thick Al-foil for solar cell applications. Properties of AZO thin film as TCO layer is not only dependent on deposition conditions (e.g., PLD) and post thermal treatment conditions (DPLR in this case) but also on substrate's properties. During single pulse DPLR processing, temperature increase per unit laser fluence applied in AZO layer is negatively correlated to the thermal conductivity (κ) of substrate; however, temperature decreasing is positively correlated to κ, which indicates that temperature accumulation occurs to low κ material when multiple pulse scheme is used. Characterization of AZO's crystal size and structural properties reveals that (1) the higher the substrate's κ is, the larger the AZO's crystal size is; (2) the better crystallinity the substrate has, the better crystallinity the recrystallized AZO has. Electrical properties including film resistivity is found to be $\sim 1.15 \times 10^{-2}\,\Omega\,\text{cm}$, the best Hall mobility measured is $196.42\,\text{cm}^2/\text{v}\cdot\text{s}$, the carrier concentration density is in the order of 10^{18}-$10^{19}\,\text{cm}^{-3}$. Compared with prior DPLR processed AZO film on SLG, electrical properties of AZO thin film is poorer on Kapton substrate. However, compared with AZO deposited on SLG with other reported methods, DPLR processed AZO on SLG has comparable film resistivity, significantly higher Hall mobility, and lower carrier concentration density. DPLR also improves AZO film's transmittance by 68% in the 1000-2000 nm range with highest improvement (177%) at 1980 nm under optimal DPLR treatment.

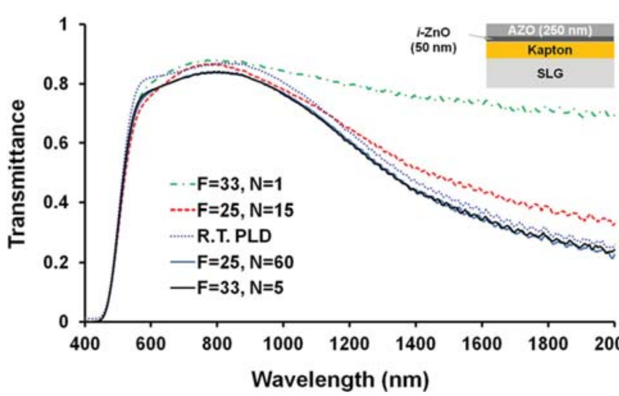

FIG. 4. Transmittance spectra of AZO films on Kapton film processed by PLD and DPLR under different conditions.

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